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The production of IF(B) in gas-phase collisions of fluorine atoms with various organic and inorganic iodides has been investigated to determine methods of efficient production. The key role of electronically-excited iodine atoms has been identified. Excimer laser photolysis of mixtures of molecular fluorine and organic iodides is shown to yield high pulse intensities of IF(B).

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COMPLETED PROJECT SUMMARY

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TITLE: The Kinetics and Dynamics of Iodine Monofluoride Formation in Gas-Phase Collisions.

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PUBLICATIONS:

"Two-photon VUV laser-induced fluorescence detection of $I^*(^2P_{\frac{1}{2}})$ and $I(^2P_{3/2})$ from alkyl iodide photodissociation at 248 nm", F.G. Godwin, P.A. Gorry, P.M. Hughes, D. Raybone, T.M. Watkinson and J.C. Whitehead, Chem. Phys. Lett., **135**, 163 (1987).

"On the role of iodine atoms in the production of IF(B $^3\Pi$) in fluorine atom / iodide flames", D. Raybone, T.M. Watkinson and J.C. Whitehead, Chem. Phys. Lett., **135**, 171 (1987).

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Chem., 8, 1988 in the press.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

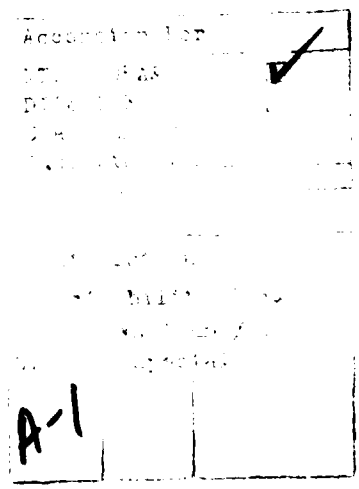
This project has concentrated on the formation of electonically excited iodine monofluoride in its B ($^3\Pi 0^+$) state with the aim of identifying high intensity sources of IF(B) for possible chemical laser work and by understanding the mechanism of IF(B) formation thereby to optimise its production. Three major experiments were undertaken with these aims.

In the first, the visible chemiluminescence (200 - 900 nm) resulting from the reactions of fluorine atoms with various organic iodides were studied in the gas-phase (~0.1 - 1.0 Torr) in a flowing system. In addition to the production of IF(B), it was found that these systems also produced CH^*, HCF^*, C_2^* and vibrationally-excited HF, except for F + CI_4, where only IF(B) was the only emitter.

In contrast, the reactions of F atoms with a range of inorganic iodides only produced IF(B) and no electronically-excited metal halides. By measuring the IF(B) vibrational population distribution, it was possible to show that IF(B) was produced by a similar mechanism in all these systems and that its precursors were ground state fluorine atoms and electronically-excited iodine atoms, $I(^2P_{\frac{1}{2}})$. This mechanism was confirmed and extended to other fluorine /iodide systems by probing the iodine atoms in the flames using two photn VUV laser-induced fluorescence and by kinetic modelling.

In the final series of experiments, it was found to be possible to generate a high intensity pulse of IF(B) by the 248 nm excimer laser photolysis of a mixture of molecular fluorine, helium and an alkyl iodide. Depending on the identity of the iodide, sustained emission from IF(B) was obtained following the laser pulse for periods between 5 and 770 μs. It is suggested that the precursors of IF(B) are again fluorine atoms and excited iodine atoms, where the fluorine atoms result from the reaction between the photolytically produced alkyl radicals and molecular fluorine and the excited iodine atoms results from the photolysis of the iodide. This method of IF(B) production would seem to hold the most promise for future chemical laser developments.

AFOSR Program Manager: Dr. Francis J. Wodarczyk



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THE KINETICS AND DYNAMICS OF IODINE MONOFLUORIDE FORMATION IN GAS–PHASE COLLISIONS

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The main purpose of this project has been to investigate methods of producing high intensities of electronically-excited iodine monofluoride in its B state, (IF(B)). IF(B) is of considerable interest because of its potential as a visible chemical laser operating in the spectral region around 600 nm. It has been calculated [1,2] that lasing could be achieved if a sufficiently high concentration of IF(B) could be obtained. Following on from earlier studies of Davis and co-workers [3] on the fluorine /iodine system, we studied [4,5] the formation of IF(B) from the gas-phase (~ 0.1 - 1.0 Torr) reactions of atomic fluorine with a range of organic iodides (CH_3I, CH_2I_2, CHI_3, CI_4, allyl iodide, iodobenzene and ortho-, meta- and para-iodotoluene). It is particularly important to the development of an IF chemical laser to find a clean source of IF(B) free from molecular iodine which has a high efficiency for quenching IF(B). In the F + organic iodide systems, as well as IF(B), a wide range of other visible emitters are also seen including CH^*, HCF^*, C_2^* and vibrationally-excited HF. Whilst of great chemical interest, this does not represent our goal of a clean source of IF(B) except for the system F + CI_4 where the only emitter observed was IF(B) enabling a measurement of its vibrational population distribution up to the predissociation limit of $v' = 9$ to be made.

The studies with the organic iodides were then extended to a range of reactions of F atoms with various inorganic iodides (BiI_3, LiI, AgI, PbI_2, HgI_2 and CdI_2) performed in the flowing system at pressures in the range 0.1 - 2.0 Torr with spectroscopic detection of the chemiluminescent products [6]. Significantly, these systems produce only electronically excited IF(B) and not the metal monohalides which makes them attractive as "clean" sources of IF(B). Of particular interest in determining the mechanism of IF(B) formation, is our observation that the vibrational population distribution of the IF(B) is non-Boltzmann in form with a significant excess population of the higher vibrational levels in the range $v' = 4 - 9$. These population distributions are essentially the same for all the inorganic iodides studied and are virtually identical to those reported [3] for the system $F_2/I_2/O_2(^1\Delta)$ where

the IF(B) is believed to be produced by pumping of high vibrational levels of ground state IF(X) by metastable $O_2(^1\Delta)$ which preferentially produces high vibrational levels of IF(B) [7]. It has been suggested [8] that an intermediate metastable state of IF, the $A'\ (^3\Pi(2))$, is involved in the energy-laddering process. However, it is our belief that this explanation of pumping by $O_2(^1\Delta)$ is incorrect.

Based on our observation that we can produce essentially identical IF(B) vibrational population distributions in a wide range of systems that do not include $O_2(^1\Delta)$ which are independent of the nature of the iodide, we have suggested that there is a universal mechanism for the production of IF(B) which must involve only very simple species that can be readily formed in all these systems. We performed further studies on the system F + BiI_3 [9] in which we investigated the role played the addition of $O_2(^1\Delta)$ to the flame. We find that the overall intensity of the IF(B) emission was increased by about an order of magnitude as was noted in the $F_2/I_2/O_2(^1\Delta)$ system [3] but the form of the IF(B) vibrational population distribution was unchanged. We have suggested that the two key precursors of IF(B) in all these F / iodide systems are fluorine atoms and electronically excited iodine atoms, $I(^2P_{\frac{1}{2}})$. IF(B) is then formed by a very fast process which is either direct recombination of I^* and F or involves the formation of IF(X) by reaction of F with the parent iodide followed by sequential collisional pumping of IF(X) to IF(B) by I^*. To confirm this hypothesis, we have used a two-photon VUV laser-induced fluorescence technique to probe the concentrations of ground and excited state iodine atoms in the F / BiI_3 flame [9]. These measurements are in agreement with a kinetic model that we have developed and give us confidence in our identification of a universal mechanism involving F and I^* for IF(B) production in these F / iodide systems.

The effect of adding $O_2(^1\Delta)$ to the F + iodine system is now easily explained as the $O_2(^1\Delta)$ is very efficient in converting ground state iodine atoms into electronically-excited

iodine atoms by a near-resonant E -> E energy transfer and that this increase in the I^* concentration increases the yield of IF(B) We have shown that it is possible to characterise the mechanism of IF(B) formation in a wide variety of gas-phase systems that produce IF(B) by examining the form of the IF(B) vibrational state distribution [10].

High intensity pulses of IF(B) have been produced following the 248 nm excimer laser photolysis of a gaseous mixture of molecular fluorine, helium and an iodide at a pressure of ~ 0.5 Torr [11,12]. The iodides used were n-C_3F_7I, C_2F_5I, CF_3I, CH_3I, C_2H_5I and t-C_4H_9I. The total intensity and decay rate of the IF(B) emission was found to be a strong function of the identity of the alkyl iodide and can be correlated with the 248 nm photon yields for the production of $I^*(^2P_{\frac{1}{2}})$ [13]. The half-lives for the IF(B) decays range from 5 μs for t-C_4H_9I to 770 μs for n-C_3F_7I. The most intense signals are for the fluoro-iodides. Decay curves for the $I^*(^2P_{\frac{1}{2}})$ concentrations are also measured by atomic fluorescence. It is suggested that IF(B) is produced in these systems either by a recombination process involving I^* and F atoms or by multistep collisional excitation of ground state IF(X) by I^*. The F atoms can be produced following the photolysis pulse by the reaction of the alkyl radical with molecular fluorine (this will be the rate determining step) and IF(X) can result either from the reaction of F atoms with the alkyl iodide or from a dark reaction between molecular fluorine and the alkyl iodide. We believe that this is the most promising of the systems that we have investigated in terms of high efficiency IF(B) generation and it is possible that it might form the basis for a photolysis-induced chemical laser (PICL). Further work needs to be done on this system to optimise IF(B) production and to determine the peak IF(B) photon yields. Future developments should concentrate on determining whether gain can be demonstrated and if it is possible to make the system lase. It was also found [14] that $CF_2(\tilde{A}\ ^1B_1)$ emitting in the spectral region 248 - 480 nm is produced in these systems, being most intense for CH_3I and t-C_4H_9I.

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Publications Resulting from this Project

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